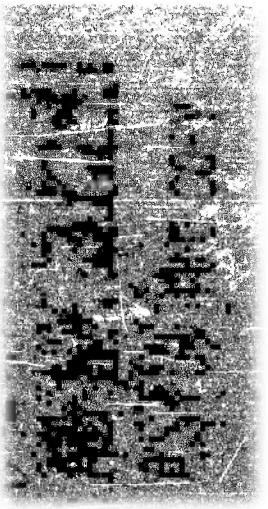


Report No. 3

on

Contract No. Nonr 495(06)
Project No. NR 037-024

George E. MacWood December 21, 1953

RF Project 553
Report No. 3

PROGRESS

R E P O R T

by

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

Columbus 10, Ohio

To: OFFICE OF NAVAL RESEARCH
DEPARTMENT OF THE NAVY, Washington 25, D.C.
Contract No. Nonr 495(06)
Project No. NR 037-024

On: PROPERTIES OF LOWER TITANIUM CHLORIDES

For the period: May 1, 1953 - November 30, 1953

Submitted by: George E. MacWood

Date: December 21, 1953

PROPERTIES OF LOWER TITANIUM CHLORIDES

Progress Report No. 3

1. INTRODUCTION

This report covers the work of the period 1 May through 30 November 1953.

2. PERSONNEL

Mr. David Clifton was added to the staff as a Research Assistant 1 July 1953.

3. VAPOR PRESSURE AND DISPROPORTIONATION OF $TiCl_3$

3.1 GENERAL

As indicated in Progress Report No. 2, titanium trichloride in the neighborhood of 600° to 700° K is involved in two simultaneous equilibria, (a) the disproportionation equilibrium:

$$2TiCl_3(s) = TiCl_2(s) + TiCl_4(g),$$

and (b) the vapor pressure equilibrium:

$$TiCl_3(s) = TiCl_3(g).$$

The Knudsen effusion method which we are using, of course, measures a function of these two pressures; namely,

$$\text{const.}\ (p_3\sqrt{M_3} + p_4\sqrt{M_4}),$$

where the constant depends on the temperature, time and orifice area, p_3, p_4 and M_3, M_4 are the pressures and molecular weights of the trichloride and tetrachloride, respectively. Therefore, in order to determine both p_3 and p_4, it is necessary either to work in a temperature range in which one is negligible compared with the other, or to make measurements by an independent method of p_3, p_4 or the total pressure. We are planning to measure p_4 independently by a spectrophotometric method (see Section 6).

What we have done up to the present is to use approximate values of p_3 supplied to us by the New Jersey Zinc Co. [1] to obtain from our measurements tentative values of p_4.

3.2 RESULTS

The graph of the logarithm of the tentative p_4 values against the corresponding values of $\frac{1}{T}$ gives a reasonably good straight line, its equation being:

$$\log p_4 = - \frac{(6.5807 \pm 0.180) \times 10^3}{T} + (7.8704 \pm 0.276)$$

for the temperature range 592.8°K $\leq$ F19.3°K. This gives a tentative value of the heat of disproportionation reaction of30.106 ± .823 Kcal/mole at an average temperature of 650°K.

It should be pointed out that these results are for runs for which the average composition of the charge varied between 2.45 and 2.98 for the molar chlorine to titanium ratio. For smaller ratios, it is found that the weight loss falls off rapidly. It is still not possible to say positively whether the falling-off is due to a surface effect or to solid solution. However, the fact that the values do not fall off until a fairly low value of the mole ratio is reached is suggestive of a surface effect, as is the observation that each charge begins to fall off at a different mole ratio.

As a method of obtaining independent information concerning p_3 we are going to carry out transpiration vapor pressure measurements on $TiCl_3$ using $TiCl_4$ as the carrier gas to suppress the disproportionation reaction. We will continue the Knudsen cell measurements using mixtures of di- and trichloride to determine the effect of mole ratios.

4. CRYSTAL STRUCTURE OF $TiCl_3$ AND $TiCl_2$

4.1 GENERAL

There is reason to believe that $TiCl_3$ and $TiCl_2$ form solid solutions with one another[1]. This led us to wonder whether or not there was any correlation between the two reported structures[2,3]. This appears to be true.

Both substances have structures that are indexed in the hexagonal system. $TiCl_3$ has the $FeCl_3$-structure, with 6 molecules per unit cell, the dimensions of which are:

$$a = 6.12 \text{ Å}, \quad c = 17.5 \text{ Å}.$$

$TiCl_2$ has the CdI_2-structure, with 2 molecules per unit cell, the dimensions of which are:

$$a = 3.56 \text{ Å}, \quad c = 5.88 \text{ Å}.$$

Both these prototype structures, $FeCl_3$ and CdI_2, are layer structures which consist of two planes of close-packed halide ions with the metal ions sandwiched between them and occupying the octahedral coordination sites. In the CdI_2-structure, all these sites are occupied, while in the $FeCl_3$-structure, only two-thirds of them are occupied. Thus, if (the proper) one-third of the metal ions of a substance which has the CdI_2-structure are removed, an $FeCl_3$-structure is obtained with a unit cell whose a-dimension is $\sqrt{3}$ times as large, whose c-dimension is 3 times as large and which has 3 times as many molecules per unit cell.

Consider the application of this process to the structure of $TiCl_2$. We obtain a substance having the stoichiometric composition $TiCl_3$ and the $FeCl_3$-structure. The new unit cell will have:

$$a = \sqrt{3} \times 3.56 = 6.17 \text{ A},$$
$$c = 3 \times 5.88 = 17.64 \text{ A},$$

and the number of molecules in the new unit cell will be $3 \times 2 = 6$. This is in very close agreement with the reported structure of $TiCl_3$. Thus the structures of $TiCl_3$ and $TiCl_2$ are very closely related. Furthermore, a structure of composition intermediate between $TiCl_2$ and $TiCl_3$ would be considered as a solid solution of $TiCl_3$ and $TiCl_2$.

There is one further observation which fits into this scheme. It has been observed(1) that x-ray powder photographs of samples, the empirical composition of which was between $TiCl_2$ and $TiCl_3$, gave identical results except that the intensity of one line (or perhaps several) varies with the composition. The same result is obtained by reconstructing the powder patterns for $TiCl_2$ and $TiCl_3$ from the powder work on the pure compounds(2,3). It is found that the patterns are very nearly identical except: a). the $TiCl_2$-pattern contains some lines absent in the $TiCl_3$-pattern (namely those reflections extinguished because the smallest $TiCl_3$ unit cell is a rhombohedron), and b). the positions of the lines are different by about 0.75% because of the slight disagreement between the cell constants.

This latter discrepancy may be real or due merely to experimental error. The question of whether or not the existence of a solid solution can be shown by x-ray diffraction data depends on whether or not this discrepancy is actual. Suppose that the lattice constants are identical. Then, as we go from $TiCl_2$ to $TiCl_3$ through a range of solid solutions, the only thing which would be observed is that the intensities of a few lines fall off and finally disappear. The same thing would be observed for mixtures of $TiCl_2$ and $TiCl_3$. However, if the constants are not identical, then, in addition to the intensity changes, the positions of the lines will shift. For the solid solution, a continuous displacement with change of average composition is to be

expected; whereas for a mixture two separate sets of lines will be involved, the intensity of one set increasing, while the other decreases. Precision powder photographs should be able to clear up this point. The data available at present are not good enough.

4.2 EXPERIMENTAL

The experimental work done up to the present consists of a set of photographs of single crystals of $TiCl_3$ made by using a Buerger precession camera.

The crystals were mounted in pyrex capillaries about the diameter of which was about 0.4 mm with a 0.02 mm wall thickness. Many mounting procedures were tried. The one finally adopted is tedious, but not very difficult. The capillaries are given a flared end, while the other end is sealed off. Working inside a dry-box, the operator transfers the desired crystal to the capillary by means of a glass rod that is electrostatically charged. After the crystal has settled as far in the capillary as possible, the open end of the capillary is sealed off temporarily with paraffin and the assembly is removed from the dry-box. After waiting several minutes for the electric charge to leak off, the capillary is tapped until the crystal wedges itself between the capillary walls. Finally the open end is sealed off permanently in a tiny gas flame. The capillary is then mounted in the usual manner on a goniometer head.

4.3 RESULTS

Nine usable precession photographs were made. Five of these were made with the x-ray beam parallel to the c-axis (i.e., perpendicular to the broad side of the crystal), covering the planes of the reciprocal lattice HKO through HK4. Four photographs were made with the beam perpendicular to the c-axis and at 30° to the a-axis, covering the planes H(-2H)L, H(-2H + 1)L, H(-2H + 2)L, H(-2H + 3)L.

The following information was obtained from these photographs:

a. The photographs have been indexed in the hexagonal system; unit cell: $a \simeq 6.17$A, $c \simeq 17.6$Å (N.B., these values are not precise)

b. Only those reflections are present for which $2H+K+L = 3n$. Here n is an integer. This indicates that the lattice is rhombohedral.

c. The HKL, HK2 and HK4 photographs indicate a three-fold axis, but no mirror plane. Hence, Laue symmetry is $C_{3i} - \bar{3}$;

d. From b and c, it follows that the space group must be $R\bar{3} - C_{3i}^{2}$ or $R3 - C_{3}^{4}$(4);

e. The volume of the unit cell is $\sim 573 \text{Å}^3$. Therefore there must be 6 molecules per unit cell.

The present work essentially confirms and extends the work and conclusions of Klemm and Krose (2).

Klemm and Krose were unable to observe lines for which $L \neq 3n$. They point out that these lines should be weak and depend on the arrangement of the titanium atoms only. If their absence is genuine (i.e., zero intensity rather than low intensity), this would indicate that the titanium atoms are not in the exact positions given by their proposed structure, but arranged statistically within the layers. This possibility of randomness in the arrangement of the titanium atoms is of interest in relation to the possibility of the formation of solid solutions.

Our precession photographs give at least a partial answer on this point. The reflections in question are actually observed. There is, however, a large amount of diffuse scattering surrounding these reflections, indicating appreciable disorder in the arrangement of the titanium atoms.

5. HEATS OF FORMATION

5.1 CALIBRATION OF THE ICE CALORIMETER

Upon completion of the ice calorimeter construction(5), the space between the inner jar and the reaction-well was filled with water and mercury. The mercury was then extended through the capillary and cooling coil to a standard taper joint which facilitated the connection to the dilatometer.

The filling process required a special apparatus. Triply distilled water was made air-free by pumping, and this was then run into the jacket which had been evacuated and flushed with water vapor several times. When the proper amount of water had been added, mercury was then run in through the capillary until the jacket contained only water and mercury. By this method, the jacket contained only air-free water and mercury, the latter being continously connected to the exterior through the mercury thread in the capillary.

The capillary bore of the dilatometer was measured by use of a weighed mercury thread. The bore varied about linearly, such that the radius could be expressed as a straight-line function. Using these data

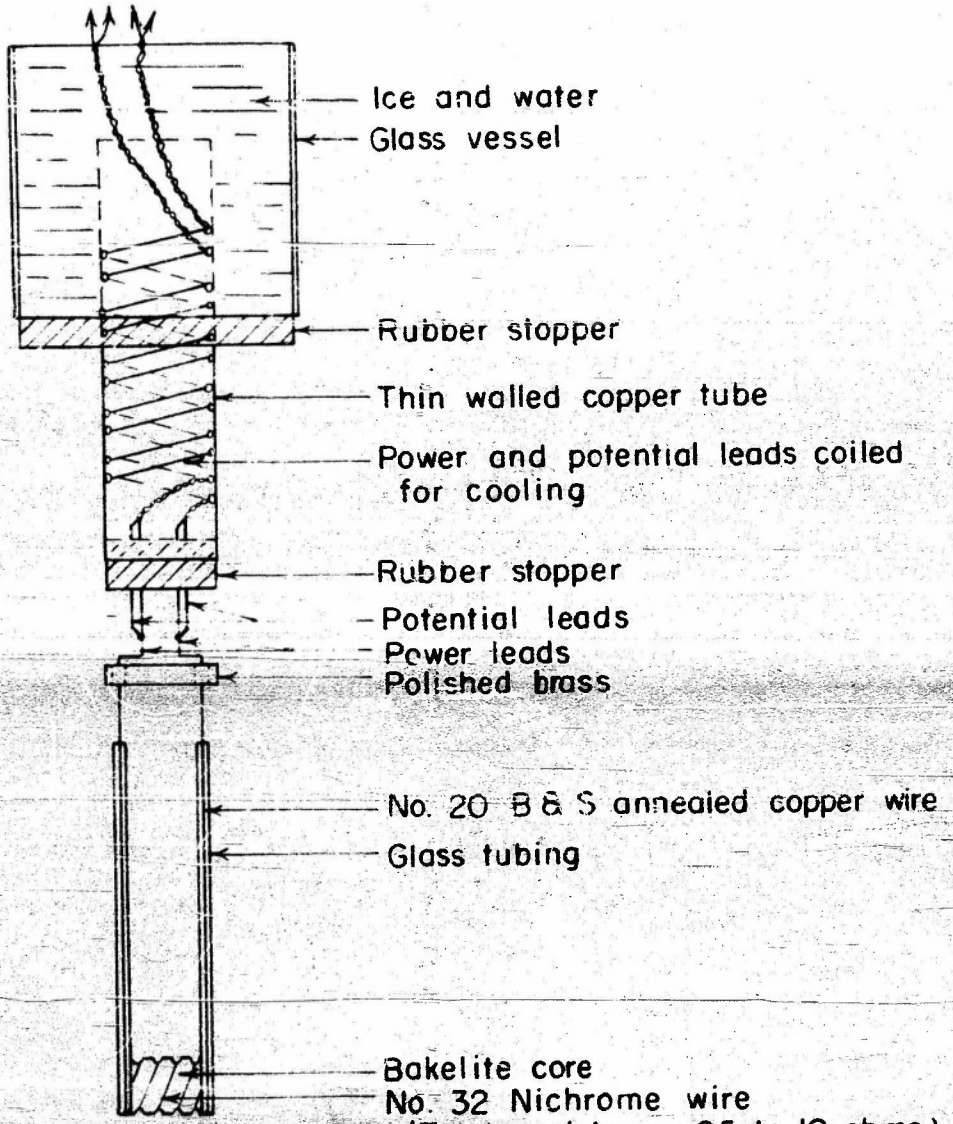
and measurements of the markings on the burette surrounding the capillary taken with a traveling microscope, the volume increments for the various markings were calculated.

The ice shelf was frozen into place by insertion of a liquid air finger, made of copper tubing, into the reaction well. The progress of freezing was controlled by moving the cold finger up and down. Observations on the ice shelf are made through a periscope-like arrangement. This method of freezing naturally gives supercooling of the ice, hence necessitates allowing the apparatus to stand for 8 to 10 hours before any readings are taken.

In order to make observations of the heat leak or addition of heat to the calorimeter, one follows the position of the mercury meniscus in the dilatometer as a function of the time. Actually the scale markings are assigned volume-values from the calculated volume-increments and these volume-values are plotted against time. One sees that when the system has attained a state of "equilibrium", the heat leak into the system is constant; i.e., the plot of volume against time gives a straight line. Now if a quantity of heat is produced in a relatively short period of time, the slope of V plotted against t increases steeply until this added heat has all been used to melt ice in the ice shelf and then the slope slowly reverts to a value the same as for the fore-period. By extrapolation of these two "equilibrium" heat-leak rates, the fore- and after-periods, to the time of addition of the heat, and subtraction of the two corresponding volumes, one obtains the volume change associated with the energy increment.

After making a number of heat-leak observations, with and without the addition of extra quantities of heat, it has been found that the most effective curves are obtained when the ice shelf is only of moderate size. The reasons for this involve several points of reasoning which will not be elaborated on at this time. Nevertheless, it has been found that for the most reliable conditions for reproduction of results in calibration it is essential to operate with a moderate size ice shelf.

For the actual calibration of the apparatus an electric heater was used to add specific amounts of heat. Diagram 1 shows the construction of the heater. The entire assembly is pre-cooled and fits into the calorimeter-well which contains pre-cooled water. During construction, the design of the heater was revised a time or two to meet experimental conditions. The power leads decided upon, No. 20 B and S annealed copper wire, were the result of a compromise between having minimum heat dissipation in the power leads, and, at the same time, having minimum thermal conduction through the leads. It was calculated that with these power leads about 0.15% of the power was dissipated in the leads. However, due to immersion of the heater and leads in water, a conservative estimate of the amount of the total heat that may not be measured in the calorimeter is only about 0.05%. The heater element was made of No. 32 Nichrome wire and had a total resistance of about 10 ohms.



HEATER AND HEAT SHUNT ASSEMBLY

DIAGRAM 1

The quantity of energy dissipated in the heater was determined by measuring the current in the heater, the voltage across the heater, and the time the heater-current was on. Diagram 2 shows the actual circuit. A Leeds and Northrup type K-2 potentiometer, a Leeds and Northrup 10 ohm standard resistor, and a Rubicon galvanometer were used to make the measurements.

The general procedure for determining the calibration factor is as follows. The ice shelf was formed and allowed to stand 8 to 10 hours to come to equilibrium. The pre-cooled heater and a quantity of pre-cooled water were put into the reaction well. The system was allowed to equilibrate for about 1-1/2 hours. The meniscus of the dilatometer was observed and readings were taken at about 4 or 5 minute intervals for about 45 minutes to 1 hour to ascertain that the heat-leak was constant. The heater was turned on, the circuit having been pre-set to deliver a certain amount of heat in a definite interval of time. While the heater was running, a series of 8 to 10 readings of the potentials across the heater and standard resistor and readings of the meniscus were taken. These latter readings were taken merely to follow the course of the proceedings. At the end of the interval when the desired amount of heat had been added, the heater was turned off. Readings were again taken of the meniscus for a period of 1-1/2 or 2 hours. The meniscus readings were converted to volume changes and plotted against the time.

By the method of least squares, the after-heat-leak curve was extrapolated to the time at which the heater was turned on. The fore-heat-leak curve was also extrapolated to this same time. By subtraction of the two volumes from the fore- and after-heat-leak curves, the volume increment corresponding to the energy input was obtained.

The energy input was obtained by using the measured potentials, time, and resistance of the standard resistor according to the equation:

$$U = \frac{E_h E_s t}{R_s} \text{ int. joules}$$

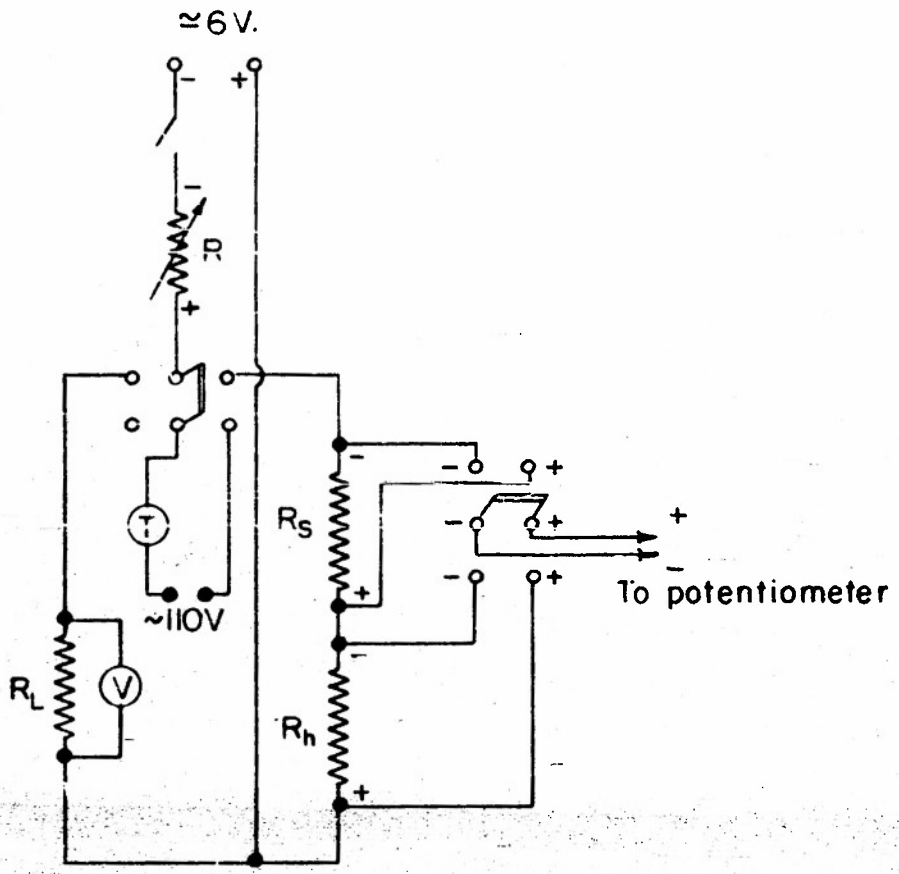
where

E_h = heater voltage (int. v.)

E_s = standard resistor voltage (int. v.)

R_s = standard resistance

t = time (sec).



R = Variable resistance

$R_L = R_S + R_h$

R_h = Heater resistance

R_S = Standard resistance – 10.000 ohms

(V) = Voltmeter

(T) = Timer (reads to 0.1 sec., can approximate .05 sec.)

WIRING DIAGRAM FOR MEASURING ENERGY INPUT

DIAGRAM 2

This was then converted to calories (defined) using the relation:

$$1 \text{ calorie} = 4.1833 \text{ int. joules.}$$

Using the calculated energy input and the determined volume increments, the apparatus constant, K, can be calculated from

$$K = U/\Delta V \text{ calories/cc.}$$

DETERMINATION OF APPARATUS CONSTANT

U calories	ΔV cc	K cal/cc
124.809	.14165	881.108
125.151	.14338	872.862
128.720	.14654	878.389
130.129	.14832	877.329
124.774	.14173	880.395
127.437	.14508	878.397

The average value of the apparatus constant was found to be:

$$K = 878.08 \pm 0.093\% \text{ calories/cc.}$$

The National Bureau of Standards[6] gives as their value of K:

$$K = 878.691 \pm 0.02\% \text{ calories/cc.}$$

As is seen, the NBS value and ours agree within the limits of our precision. The NBS calibration was done upon a similar calorimeter, but they used quantities of heat 5 to 50 times those used here and employed a weighing method to determine volume displacement. The calorimeter used was also designed primarily for calibration purposes.

Two factors that influence the precision of the results in this work are the quantity of heat used in a determination, as this in turn determines the volume change measured, and the accuracy of determining the volume change.

As the data show, the heat quantities were approximately 125 calories and involved volume increments of about 0.142 cc. Considering the bore of the capillary it follows that to measure 0.142 cc within 0.1%, it is necessary to measure the meniscus displacement to about 0.4 mm. This means in the readings and the necessary extrapolations not much error is allowed in obtaining ΔV to 0.1%.

Prior to obtaining these results, many calibration attempts were made which gave varying results. In these runs there were wide variations in the size of the ice shelf which gave differences in the heat-leak rates. Sometimes the leak rates were steep, somewhat irregular, and generally not conducive to effective extrapolations. These runs were made with small heat-inputs which resulted in making small errors in extrapolation a large percentage of the total volume change. Upon revising the technique by using moderate and closely similar ice shelves, as well as larger energy inputs, a marked improvement in consistency was obtained with the results reported above.

6. OPTICAL ABSORPTION OF TITANIUM CHLORIDE VAPORS

6.1 GENERAL

As indicated in Section 3, it would be desirable to have an independent method of measuring the pressure of titanium chloride. In other connections, it would be important to have a method of measuring the pressure of the other chlorides. We have, therefore, begun an investigation of the optical absorption of the chloride vapors.

6.2 RESULTS

With the aid of a Beckman DU spectrophotometer, we have made several runs in order to determine the optical density of titanium chloride vapor for several pressures as a function of wavelength. The results are shown in Figure 3 and indicate that the spectrophotometric method can be used for $TiCl_4$, provided no other species present interfere.

We have designed an apparatus for the spectrophotometric investigation of the vapor phase in equilibrium with various solid phases, in connection with the disproportionation equilibria. Its construction is very nearly completed. Results obtained with it will be given in the next progress report.

7. REFERENCES

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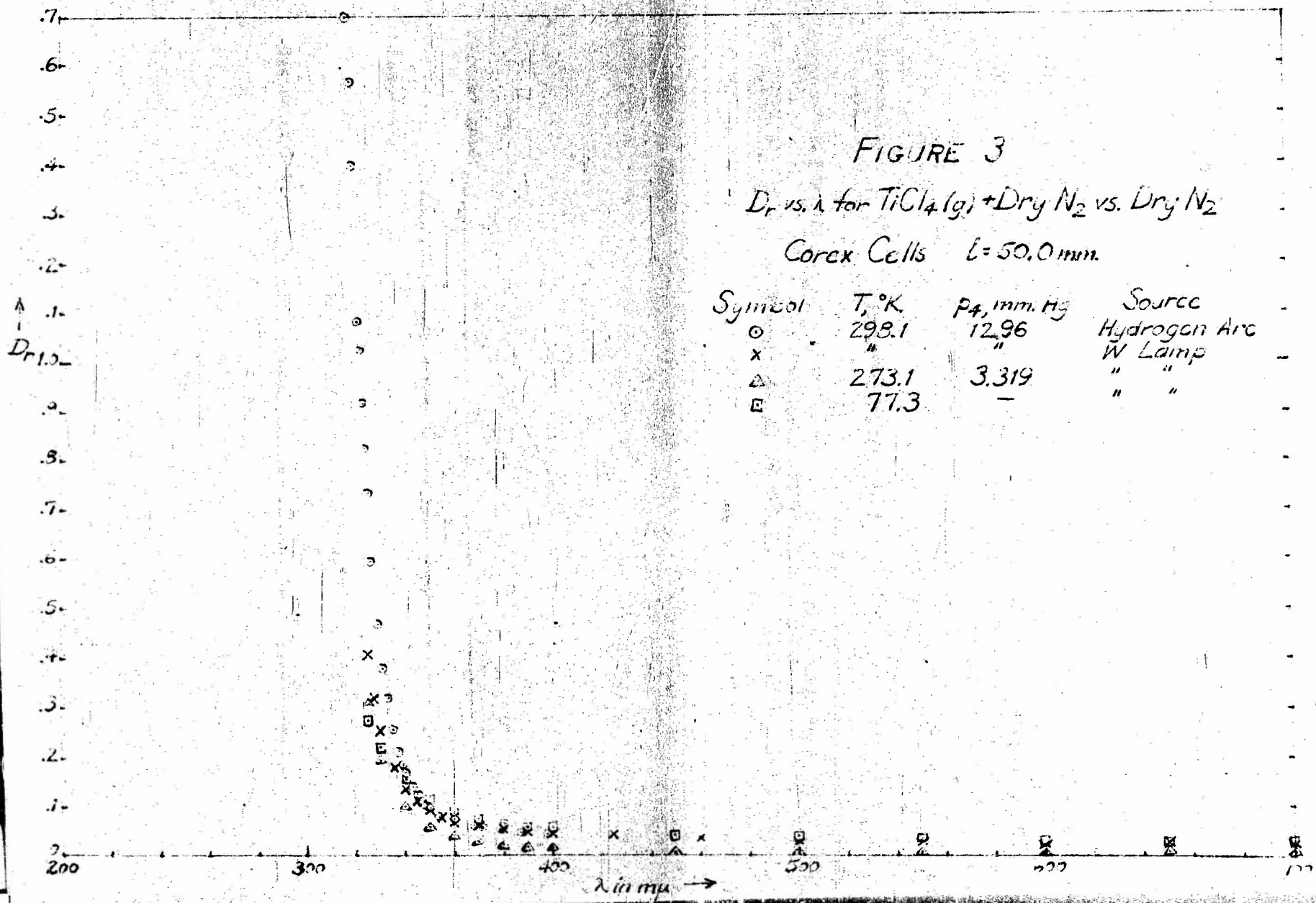

FIGURE 3

D_r vs. λ for $TiCl_4$ (g) + Dry N_2 vs. Dry N_2

Corex Cells ℓ = 50.0 mm.

Symbol	T, °K.	P_4, mm. Hg	Source
⊙	298.1	12.96	Hydrogen Arc
×	"	"	W Lamp
△	273.1	3.319	" "
⊡	77.3	—	" "

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to

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Investigator J. E. MacDonald Date 1/5/54

Supervisor E. MacDonald Date 1/6/54

For The Ohio State University Research Foundation

Executive Director Sponsored Research Date 1/6/54